



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number:

**0 245 928 B1**

(12)

## EUROPEAN PATENT SPECIFICATION

- (45) Date of publication of patent specification: **26.01.94** (51) Int. Cl.<sup>5</sup>: **A01N 37/02, A01N 37/04, A01N 37/06**
- (21) Application number: **87302215.6**
- (22) Date of filing: **16.03.87**

(54) **Antimicrobial compositions.**

- (30) Priority: **17.03.86 US 840336**  
**02.03.87 US 20367**
- (43) Date of publication of application:  
**19.11.87 Bulletin 87/47**
- (45) Publication of the grant of the patent:  
**26.01.94 Bulletin 94/04**
- (84) Designated Contracting States:  
**AT BE DE ES FR GB IT NL SE**
- (56) References cited:  
**EP-A- 0 135 898**  
**WO-A-83/00163**  
**DE-A- 3 229 097**  
**GB-A- 1 504 847**  
**US-A- 4 277 378**

- (73) Proprietor: **Diversey Corporation**  
**1 Robert Speck Parkway,**  
**Suite 1600**  
**Mississauga, Ontario L4Z 3S9(CA)**
- (72) Inventor: **Stanton, James H**  
**21575 Canterbury**  
**Gross Ile Michigan 48138(US)**  
Inventor: **Lichorat, James L**  
**9880 Church Road**  
**Gross Ile Michigan 48238(US)**  
Inventor: **Lopes, John A**  
**8469 Concord**  
**Gross Ile Michigan 48238(US)**
- (74) Representative: **Froud, Clive et al**  
**Elkington and Fife**  
**Prospect House**  
**8 Pembroke Road**  
**Sevenoaks, Kent TN13 1XR (GB)**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

**EP 0 245 928 B1**

## Description

This invention relates to novel coupling agents which increase the stability of antimicrobial sanitizing and cleaning or detergent compositions, and in particular their use in a novel cleaning and sanitizing or detergent composition containing n-alkyl and/or n-alkenyl succinic acids as an active antimicrobial agent.

Various chemicals exhibit varying degrees of antimicrobial activity. Among these are short-chain monocarboxylic acids having less than twenty carbon atoms, quaternary ammonium compounds and hexachlorophene compounds. These compounds have been admixed with various surfactants and water to yield aqueous sanitizing solutions.

It has been found that the antimicrobial activity of these compounds can be increased when the sanitizer solution is acidified to a pH below about 5. Acid sanitizing solutions of this type are generally employed in food, beverage, brewery and other industries as a clean-in-place sanitizing solution for processing equipment.

Generally, antimicrobial solutions containing these antimicrobial agents are undesirable for use in food equipment cleaning applications. Residual amounts of the acid sanitizing solutions which remain in the equipment after cleaning can impart unpleasant tastes and odors to food. The cleaning solutions are difficult to rinse from the cleaned surfaces. Larger amounts of water are required to effectively completely remove conventional sanitizing solutions. Those sanitizers containing halogens can be corrosive to metal surfaces of food plants. Quaternary ammonium compounds strongly adhere to sanitized surfaces even after copious rinsing and may interfere with desired microbial growth during food processing; e.g. fermentation.

It has, also, been found that the antimicrobial activity of conventional acid sanitizing solutions can be adversely affected by the hardness of the water used in and with the solution. A marked decrease in antimicrobial activity has been noted at water hardness above about 500 ppm. Therefore, in order to assure sufficient antimicrobial activity, the hardness of water must be carefully adjusted to maintain the hardness below about 500 ppm.

The acid sanitizing solutions presently available are effective against gram negative and gram positive bacteria such as *E. coli* and *Staph. aureus* but are not as efficacious on any yeast contamination which can be present. In many applications control of yeast infestations requires a separate solution than that which is used to eliminate gram negative and gram positive bacteria. Use of two solutions can be costly and time consuming.

Such antimicrobial solutions are, generally, produced by admixture of water and an aqueous concentrate containing antimicrobial agents, water or other suitable diluents and acids capable of yielding a pH below about 5 upon dilutions. As can be appreciated, such antimicrobial concentrate compositions must exhibit homogeneity and solution stability during prolonged storage periods; particularly at low temperatures. To achieve this, solubilizers or coupling agents are added to the concentrate to maintain stability of the solution at high acid concentrations at prolonged low temperatures or during repeated freeze/thaw cycles.

Such solubilizers are, generally, surfactant hydrotropes capable of solubilizing the antimicrobial agent in the acidic concentrate which maintaining it in active form in both the concentrate and in the diluted antimicrobial solution suitable for conventional use. Various anionic, zwitterionic and nonionic surfactants or mixtures thereof have been previously employed in such solutions.

These solubilizers, when used in antimicrobial compositions, tend to cause undesirable foaming, thus requiring the addition of foam suppressants. Additionally, these solubilizers did not provide stability of the antimicrobial concentrate compositions over a wide range of storage temperatures.

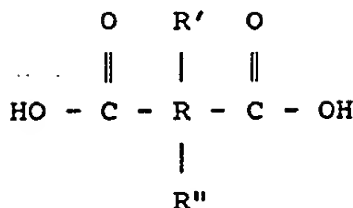
Thus, it is desirable to provide a stable antimicrobial concentrate which can provide an antimicrobial solution which is equally effective on gram negative and gram positive bacteria and on yeast. It is desirable that the antimicrobial activity of the solution be unaffected by water hardness. It is also desirable that the composition provide a low-foaming antimicrobial use solution.

In accordance herewith, there is provided an antimicrobial sanitizing composition which is capable of being diluted with a major amount of a food grade diluent to form an antimicrobial use solution. The composition hereof comprises:

(a) an antimicrobial agent selected from a monocarboxylic acid, a dicarboxylic acid and mixtures thereof, the monocarboxylic acid having the general formula:



wherein  $R'''$  is a straight or branched, saturated or unsaturated alkyl moiety having between about 6 and about 12 carbon atoms, the dicarboxylic acid having the general formula:



wherein R is a saturated or unsaturated hydrocarbon moiety having 2 carbon atoms; R' is a substituted or unsubstituted n-alkyl or n-alkenyl moiety each n-alkyl or n-alkenyl moiety having about 6 to about 12 carbon atoms or R' is diisobutenyl or methyl heptenyl; and R'' is a functional group selected from hydrogen and hydroxy; where R' is substituted, suitable substituents include thiols, methane thiols, amines, methoxy compounds and various aromatic compounds;

(b) a solubilizer selected from an alkyl N,N-dimethyl amine oxide solubilizer-coupling agent having between about 8 and about 10 carbon atoms in the alkyl portion thereof;

(c) an anionic diluent; and

(d) an acid capable of yielding a solution pH less than or equal to 5.0 upon dilution of the composition to use solution.

The present invention also provides an antimicrobial "use solution" which is particularly suited for "in place" cleaning. The use solution comprises water and the anionic diluent and provides:

- (a) between about 10 and about 500 parts per million (ppm) of the selected antimicrobial agent;
- (b) between about 10 and about 500 ppm of the solubilizer; and
- (c) sufficient of the acid to yield a pH below about 5.

Using the dilute composition in cleaning "in place" systems, such as are found in dairies and breweries, involves the circulation of the sanitizing solution through the system at ambient temperatures followed by an optional rinse phase with potable water. The sanitizing composition may also be used in a detergent composition to provide a sanitizing action in association with a detergent cleaning process.

The type and amount of the above-listed components can be varied so that compositions have the effectiveness and characteristics desired.

For a more complete understanding of the present invention, reference is made to the following detailed description and accompanying examples.

The antimicrobial sanitizing composition of the present invention is predicated on the unexpected discovery that certain dicarboxylic acids exhibit enhanced antimicrobial activity, at pH levels at or below about 5.0.

The antimicrobial sanitizing composition of the present invention is further predicated on the discovery that certain alkyl derivatives of amine oxides provide enhanced solubilizing action in concentrated acidic solutions containing antimicrobial agents such as monocarboxylic acids and dicarboxylic acids, without increasing the foaming action of diluted use solutions made therefrom. It has also been found that those substituted amine compounds enhance the low- and high-temperature stability of antimicrobial compositions in which they are employed.

The term "sanitizing" as used herein to indicate reduction of undesirable microorganisms by about five orders or magnitude or greater within time periods set forth below.

The composition, generally, comprises:

- (a) from about 0.25 to about 25 percent, by weight, of the defined antimicrobial agent, based on the total weight of the composition;
- (b) from about 0.25 to about 40.0 percent, by weight, based on the total weight of the composition, of the defined solubilizer;
- (c) from about 10.0 to about 95.5 percent, by weight, based on the total weight of the composition, of the diluent; and
- (d) from about 4.0 to about 50.0 percent, by weight, based on the total weight of the composition, of the defined acid.

The present composition as well as the use solution made therefrom can incorporate other conventional antimicrobial agents such as quaternary ammonium compounds etc. Also, various dyes, perfumes, etc. can be employed either in the present composition or the use solution.

The antimicrobial sanitizing composition of the present invention in its more concentrated form can be effectively diluted with water or another suitable diluent such as various short-chain alcohols to provide a

use solution having between about 10 ppm and about 500 ppm of the carboxylic acid antimicrobial agent while maintaining the pH at or below 5.0 without compromising the effectiveness of the solution.

In practicing the present invention, and as noted hereinabove, the antimicrobial agent may be either a mono- or dicarboxylic acid. Preferably, the dicarboxylic acid is employed.

5 The preferred dicarboxylic acids employed in the present invention are those having a four-carbon saturated or unsaturated backbone.

Without being bound to any theory, the unexpected efficacy of the dicarboxylic acid moiety over monocarboxylic equivalents appears to be related to the lower vapor pressures of the dicarboxylic acid moieties. The lower vapor pressures aid in keeping the resulting sanitizer use solution free from undesirable  
10 organoleptic properties associated with organic acids. Furthermore, it appears that straight-chain unsaturation increases the solubility of the material in an aqueous environment without adversely affecting antimicrobial properties.

Specifically, the dicarboxylic acids employed herein are selected from the group consisting of succinic acid, maleic acid and fumaric acid, and preferably, succinic acid. The preferred succinic acids employed in  
15 the present invention are selected from the group consisting of n-octyl succinic acid, n-octenyl succinic acid, n-nonyl succinic acid, n-nonenyl succinic acid, n-decyl succinic acid, n-decenyl succinic acid, n-hexyl succinic acid, n-hexenyl succinic acid, diisobutenyl succinic acid, methyl heptenyl succinic acid and mixtures thereof.

It has also been found that admixture of dicarboxylic acids with certain short-chain monocarboxylic  
20 acids can also be efficacious in antimicrobial compositions of this type. Preferred monocarboxylic acids are selected from the group consisting of capric acid, caprylic acid, neodecanoic acid, decanoic acid, octanoic acid, 2,2 dimethyl octanoic acid and mixtures thereof.

It is to be understood however, and it is also within the purview of this invention to employ monocarboxylic acids independently as the antimicrobial agent in admixture with a preferred solubilizer  
25 alkyl N,N-dimethyl amine oxide having between about 6 and about 10 carbon atoms in the alkyl portion.

The solubilizer employed herein is a surfactant hydrotrope capable of solubilizing the mono- and/or dicarboxylic acid in an acidic diluent while maintaining the carboxylic acid in solubilized form in both the concentrate and the diluted use solution of the product under use conditions. Various nonionic surfactants  
30 or mixtures thereof can be successfully employed in the present invention. The preferred nonionic surfactant is the alkyl N,N-dimethyl amine oxide.

The alkyl N,N-dimethyl amine oxide solubilizing agent employed herein is a compound capable of solubilizing the antimicrobial agent in an acidic diluent while maintaining the agent in active form in both the concentrate and the diluted use solution of the product under use conditions. Various alkyl N,N-dimethyl  
35 amine oxides can be successfully employed in this invention. These compounds have been found to have greater solubilizing ability than conventional solubilizing agent have been found to be low-foaming when used in antimicrobial use solutions such as those of the present invention. Additionally, such compositions remain clear and stable over a broad range of temperatures from about -10 °F to about 120 °F (from about -23 °C to about 49 °C).

The alkyl N,N-dimethyl amine oxide solubilizing agents useful herein have between 6 and 10 carbon  
40 atoms in the alkyl portion. Preferably the alkyl component has between 8 and 10 carbon atoms. These preferred compounds are, respectively, octanamine, N,N-dimethyl-, N-oxide and 1-decanamine, N,N-dimethyl-, N-oxide. The particular preferred amine oxide is octanamine, N,N-dimethyl-, N-oxide because of its lower foam characteristics. The amine oxides contemplated for use herein are commercially available from Sherex Corporation as a 47.4 percent amine oxide solution sold under the trademark SHEREX EPSC  
45 192-65 and EPSC 192-64, respectively. These materials provide antimicrobial sanitizer compositions with low foaming action and good broad range temperature stability. Furthermore, the material can be used as a total substitute for anionic, nonionic or zwitterionic surfactants previously employed in antimicrobial sanitizers of this type; thus eliminating unpleasant odours associated with the use of such conventional surfactants.

50 The anionic diluent employed is, preferably, potable drinking water. However, other compatible diluents such as C-1 to C-3 short-chain alcohols, may be employed.

As noted hereinabove, the antimicrobial sanitizing concentrate of the present invention also contains an acid capable of providing a solution pH at or below about 5.0 when the concentrate is diluted to its use solution strength. The acid employed must be compatible with the other components of the antimicrobial  
55 sanitizing solution; i.e., it must not produce instability or cause degradation or deactivation of the surfactant or dicarboxylic acid. The acid can be either a weak organic acid such as acetic acid, hydroxyacetic acid, citric acid, tartaric acid, maleic acid, fumaric acid or mixtures thereof or an inorganic acid such as phosphoric acid, sulfuric acid, sulfamic acid or mixtures thereof. Preferably, phosphoric acid is employed.

The concentrate hereof is, generally, prepared by mixing the components together at ambient conditions, with heating, if necessary.

The concentrate hereof, as noted, is capable of forming a use solution when the concentrate is admixed with an anionic diluent such as water. The use solution thus formed generally comprises:

- 5 a) from about 10 parts per million (ppm) to about 500 ppm of the defined antimicrobial agent;
- b) from about 10 ppm to about 500 ppm of the defined solubilizer;
- c) the anionic diluent originally present in the concentrate;
- d) quantities of the organic or inorganic acid noted above sufficient to yield a use solution pH below about 5.0; and
- 10 e) water as the balance of the composition.

The antimicrobial sanitizing composition of the present invention may be successfully employed in sanitizing and disinfecting fixed-in-place food processing facilities such as those found in dairies, breweries and beverage plants. The composition of the present invention exhibits antimicrobial activity at ambient temperature.

- 15 To sanitize, the diluted use solution is circulated through the system for an interval sufficient to contact and kill undesirable microorganisms. This can be anywhere from less than about 30 seconds to about 10 minutes depending on the type and amount of contamination present. Ordinarily, the contact-time will be in the range of about one minute to about two minutes. After sanitizing, the sanitizing composition is drained from the system.

- 20 In most cleaned-in-place applications, the system can be brought back into service immediately after the sanitizing solution is removed. However, the system may be rinsed with potable water or any other suitable material after sanitizing.

- It is also appreciated that the sanitizing concentrate may be admixed with a detergent composition to impart the additional sanitizing properties of this invention to a detergent when in use. For example, detergents are routinely used in European countries to clean various facilities in dairies, breweries and beverage plants and thereby avoid the need for a subsequent sanitizing rinse of the facility. It is also appreciated that the sanitizing concentrate may be used in other ways such as in track lubricants, teat dips and ware washing rinse aids. When the sanitizing concentrate is used in a detergent composition, appropriate surfactants are employed which are preferably of the nonionic low foaming type. It is understood that such surfactant of the detergent has to be compatible with the sanitizing concentrate so as to avoid inducing degradation or separation in the final product.
- 25
- 30

For a more complete understanding of the present invention, reference is made to the following examples. The examples are to be construed as illustrative and not limitative of the present invention.

#### 35 EXAMPLE I

- Decyl succinic acid was prepared from decyl succinic anhydride by thermal hydrolysis. Two solutions of decyl succinic acid were prepared. A quantity of 75 percent phosphoric acid was added to one of the decyl succinic acid solutions such that the resulting solution contained 1 percent decyl succinic acid and 16 percent phosphoric acid. The remaining decyl succinic acid solution contained 1 percent succinic acid with no additives.
- 40

- A one-part sample of the acidified decyl succinic acid solution was admixed with 100 parts of water having 500 ppm synthetic water hardness present as calcium carbonate to yield a solution containing 100 ppm decyl succinic acid. The resulting sanitizing solution was exposed to challenge bacteria Staphylococcus aureus ATCC 6538 and Escherichia coli ATCC 11229 to determine antimicrobial effectiveness. The test procedure employed was the Germicidal and Detergent Sanitizer Test recommended by the Association of Official Analytical Chemists. The test was carried out at 77 °F (25 °C) and the results are found in Table I.
- 45

- A 50 ppm sample and a 25 ppm sample of the diluted acidified decyl succinic acid solution were prepared by admixing 0.5 part and 0.25 part samples of acidified 1 percent decyl succinic acid solutions, respectively, with 100 parts water containing 500 ppm hardness present as calcium carbonate (CaCO<sub>3</sub>). The samples were exposed to the challenge bacteria E. coli and Staph. aureus, according to the A.O.A.C. test procedures outlined above. The results are found in Table I.
- 50

- A sample containing 100 ppm of the non-acidified decyl succinic acid sample was also prepared using water having 500 ppm hardness and was exposed to the challenge bacteria. The resulting data is also found in Table I.
- 55

As can be seen from the data in Table I, the decyl succinic acid solution exhibited bacteriocidal activity under acidic conditions.

TABLE I  
Evaluation of Antimicrobial Activity of Decyl Succinic Acid

Formulation (% by weights)	Dilution (mls of Formulation per 100 ml water)	Amount of Succinic Acid Derivative (ppm)	Percent Kill at given intervals	
			Staph. aureus	E. coli
a. 1 percent decyl succinic acid in water	1.0	100	30 sec. 60 sec.	30 sec. 60 sec.
			<99.99 <99.99	<99.99 <99.99
			>99.999 >99.999	>99.999 >99.999
b. 1 percent decyl succinic acid with 15 percent phosphoric acid in water	1.0	100	>99.999 >99.999	>99.999 >99.999
			>99.999 >99.999	>99.999 >99.999
			>99.999 >99.999	>99.999 >99.999
	0.5	50	>99.999 >99.999	>99.999 >99.999
			>99.999 >99.999	>99.999 >99.999
			>99.999 >99.999	>99.999 >99.999
	0.25	25	>99.999 >99.999	>99.999 >99.999
			>99.999 >99.999	>99.999 >99.999
			>99.999 >99.999	>99.999 >99.999

## EXAMPLE II

Minimum inhibitory concentrations (mic) of n-alkenyl succinic acid derivatives effective against gram positive microorganisms were determined using differing concentrations of n-octenyl succinic acid and n-

deceeryl succinic acid in 10 ml of nutrient broth for tests against Staph. aureus and Saboraud's broth for tests against Saccharomyces cerevisiae. These concentrations of succinic acid derivatives were inoculated with 0.1 ml of a 1 to 100 dilution of the challenge cultures. The challenged concentrations were incubated for 24 hours at 37°C in the case of Staph. aureus and 30° C in the case of Saccharomyces cerevisiae.

5 Presence or absence of growth was recorded.

The results collected in Table II indicate that n-octenyl succinic acid has a minimum inhibitory concentration of 1000 ppm against Staph. aureus. N-deceeryl succinic acid showed a minimum inhibitory concentration of 1000 against Staph. aureus and 500 ppm against Saccharomyces cerevisiae.

TABLE II  
Inhibition of Gram Positive Microorganisms  
by Succinic Acid Derivatives at Various Concentrations

	n-Decenyl succinic acid				
	50 ppm	100 ppm	250 ppm	500 ppm	1000 ppm
<u>Staph. aureus</u>	+	+	+	+	-
<u>Saccharomyces cerevisiae</u>	+	+	+	-	-
	n-Octenyl succinic acid				
	50 ppm	100 ppm	250 ppm	500 ppm	1000 ppm
<u>Staph. aureus</u>	+	+	+	+	-
<u>Saccharomyces cerevisiae</u>	+	+	+	+	+
+ indicates growth					
- indicates no growth					

### Example III

In order to determine the effectiveness and stability of antimicrobial concentrate compositions containing conventional solubilizer-coupling agents, two compositions were paired, the formulae of which are set forth in Table III and designated as Compositions E and F.

Use solutions made from Compositions E and F were prepared in which the ratio of concentrate composition was 1 oz. concentrate to 4 U.S. gallons water and 1 oz. concentrate to 6 U.S. gallons water, (28.35g concentrate to 15.144l water and 28.35g concentrate to 22.716l water) respectively. Both use solutions exhibited antimicrobial activity.

A sample of Composition E, the 4x sample, was then tested at a variety of temperatures to determine its low-temperature stability. The composition became unhomogenous at 40°F (4.4°C). Because of this, the more concentrated composition, Composition F, was not tested.

A sample of Composition E was also frozen to determine the effects of a freeze/thaw cycle on this material. The material was unstable during freeze/thaw. Because of this, the more concentrated sample was not tested.

As can be observed from these test, antimicrobial concentrates containing sodium xylene sulphonate have certain instability problems which can hamper their general usefulness.

TABLE III

Materials	Composition E (wt. %)	Composition F (wt. %)
OSA <sup>1</sup>	8	9.1
SXS, 95x <sup>2</sup>	8	15.0
Phosphoric Acid, 75x	45	40.0
Water	39	27.8
C-8, C-10 fatty acid	-	8.0

<sup>1</sup>octenyl succinic acid

<sup>2</sup>sodium xylene sulfonate

#### EXAMPLE IV

A variety of antimicrobial concentrate compositions were prepared employing n-octenyl succinic acid in combination with either sodium xylene sulfonate, sodium 1-octane sulfonate or octanamine, N,N-dimethyl-N-oxide (ODI) as the solubilizer coupling agent. The amounts of solubilizer-coupling agent listed in Table IV are the minimum amounts necessary to obtain stable concentrates at room temperature. Each sample was, then, checked for stability by storing at 120°F, 40°F and -10°F (49°C, 4.4°C and -23°C). As can be seen from the results set forth in Table IV, stability was achieved with lower levels of ODI. Additionally, the samples containing ODI were the only samples stable over these temperature ranges.

Foam levels at use concentrations of 0.2 percent were compared using two foam tests, the results of which are summarized in Table IV. In the first foam test, 100 ml of each 0.2 percent use solution were placed in a 250 ml of graduated cylinder. The cylinder was then inverted 10 times. Foam levels were measured immediately after the inversions and again after a 30 second interval had elapsed. The foam heights are recorded in Table IV. As can be seen from the data collected therein, ODI exhibited the lowest foaming characteristics.

Foam results were also compared with the dynamic foam tester. In this method a small pump having a capacity of 2,600 ml/min. is used to pump solution out of a plastic chamber having a three-inch (7.62 cm) diameter, through a one-quarter inch (0.635 cm) orifice and back into the three-inch (7.62 cm) diameter chamber. Foam height is measured after 30 seconds of circulation. The results are shown in Table IV. As can be seen from this data, ODI exhibited foaming tendencies equal to those with sodium xylene sulfonate. It was also established that ODI did not detract from the antimicrobial properties of the selected antimicrobial agents.



TABLE IV

COMPARISON OF STABILITY AND FOAMING.  
CHARACTERISTICS OF VARIOUS ANTIMICROBIAL COMPOSITIONS

Concentrate Formulation	G wt%	H wt%	I wt%	J wt%	K wt%	L wt%
Sanitizing Agent:						
n-octenyl succinic acid	9.0	9.0	9.0	9.0	9.0	9.0
capric-caprylic acid				2.0	2.0	2.0
Solubilizer-Coupling Agent:						
sodium xylene						
sulfonate (40%)	25.0			30.0		
sodium 1-octane						
sulfonate (40%)		36.0			38.0	
octanamine, N,N,- dimethyl N-oxide (47%) (ODI)			18.0			17.0
Phosphoric Acid (75%)	55.0	55.0	55.0	50.0	50.0	50.0
Water	11.0	-	18.0	9.0	-	22.0
Stability: at RT	C <sup>1</sup>	C <sup>1</sup>	C <sup>1</sup>	C <sup>1</sup>	C <sup>1</sup>	C <sup>1</sup>
120°F (49°C)	St <sup>2</sup>	St <sup>2</sup>	St <sup>2</sup>	St <sup>2</sup>	St <sup>2</sup>	St <sup>2</sup>
40°F (4.4°C)	St	Sep	St	St	Sep	St
-10°F (-23°C)	Sep	Sep	St	St	Sep	St
Foam Shake Test (0.2%)	30cc	50cc	5cc	20cc	60cc	10cc
After 30 seconds	0	30cc	0	0	20cc	0
Foam Pump Test (0.2%)						
After 30 seconds	2in (5.08 cm)	12in (30.48 cm)	3in (7.62 cm)	2in (5.08 cm)	12in (30.48 cm)	2in (5.08 cm)
C = Clear						
St = Stable						

## EXAMPLE V

Another series of concentrate formulae were prepared to prove the merits of ODI. Antimicrobial concentrates containing admixtures of n-octenyl succinic acid and C<sub>8</sub>-C<sub>10</sub> monocarboxylic acids were prepared using the solubilizer-coupling agents discussed in Example III. Three formulae were prepared which all had an additional 2 percent Emery 6358 (a 40 percent capric - 60 percent caprylic food grade fatty acid blend). The minimum amounts of solubilizer-coupling agent necessary to obtain clear stable concentrate at room temperature. As is demonstrated by this data, significantly less ODI was required to obtain a stable concentrate.

As in Example III, each sample was stored at 120°F, 40°F and -10°F (49°C, 4.4°C and -23°C) Stability at these temperatures again showed the excellent stabilizing power of ODI.

Foam levels were compared using the methods outlined in Example III. The results are shown in Table IV. As can be seen from these results, ODI causes less foaming than the sulfonate solubilizers.

It is to be appreciated from the preceding that there has been described herein a sanitizer concentrate and use solution which is efficacious in killing off both gram negative and gram positive bacteria as well as

yeasts.

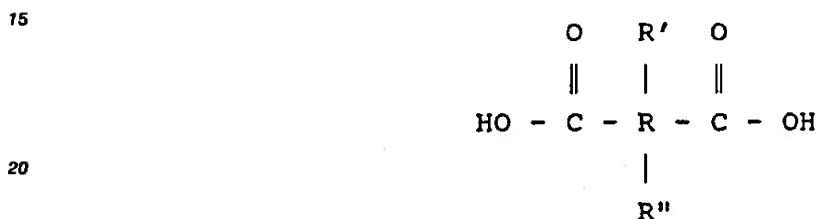
# Claims

- 5 1. An antimicrobial composition, which retains its antimicrobial action on dilution, characterized in that it comprises:

(a) an antimicrobial agent selected from a monocarboxylic acid, a dicarboxylic acid and mixtures thereof, the monocarboxylic acid having the general formula:



wherein  $R'''$  is a straight or branched, saturated or unsaturated alkyl moiety having between 6 and 12 carbon atoms, the dicarboxylic acid having the general formula:



25 wherein R is a saturated or unsaturated hydrocarbon moiety having 2 carbon atoms; R' is a substituted or unsubstituted n-alkyl or n-alkenyl moiety each n-alkyl or n-alkenyl moiety having 6 to 12 carbon atoms or R' is diisobutenyl or methyl heptenyl; and R'' is a functional group selected from hydrogen and hydroxy;

(b) a solubilizer selected from an alkyl N,N-dimethyl amine oxide solubilizer-coupling agent having between 8 and 10 carbon atoms in the alkyl portion thereof;

30 (c) an anionic diluent; and

(d) an acid capable of yielding a solution pH less than or equal to 5.0 upon dilution of the composition to use solution.

- 35 2. A composition according to claim 1 wherein it comprises:

(a) from 0.25 to 25.0 percent, by weight, of the antimicrobial agent;

(b) from 0.25 to 40 percent, by weight, of the solubilizer;

(c) from 10.0 to 95.5 percent, by weight, of the anionic diluent; and

(d) from 4.0 to 50.0 percent, by weight, of the acid;

the percentages being based on the total weight of the composition.

- 40 3. A composition according to claim 1 or claim 2 wherein each R' is a linear hydrocarbon.

4. A composition according to any of claims 1 to 3 wherein each R' has between 8 and 10 carbon atoms.

- 45 5. A composition according to claim 1 wherein each R' is a substituted moiety, the substituent being selected from thiol groups, methane thiol groups, amine groups, methoxy groups, aryl groups and mixtures thereof.

- 50 6. A composition according to any of claims 1 to 5 wherein the dicarboxylic acid is selected from n-octyl succinic acid, n-octenyl succinic acid, n-nonyl succinic acid, n-nonenyl succinic acid, n-decyl succinic acid, n-decenyl succinic acid, n-hexyl succinic acid, n-hexenyl succinic acid and mixtures thereof.

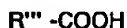
7. A composition according to any of claims 1 to 5 wherein the antimicrobial agent is selected from succinic acid, maleic acid and fumaric acid and mixtures thereof.

- 55 8. A composition according to any of claims 1 to 7 wherein the acid is a weak organic acid selected from acetic acid, hydroxyacetic acid, citric acid, tartaric acid, maleic acid, fumaric acid and mixtures thereof.

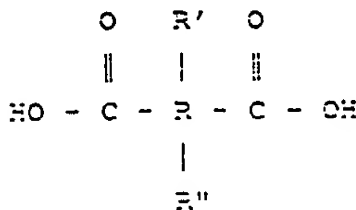
9. A composition according to any of claims 1 to 7 wherein the acid is an inorganic acid selected from phosphoric acid, sulfuric acid, sulfamic acid and mixtures thereof.
10. A composition according to any of claims 1 to 7 wherein the acid is a mixture of an inorganic acid and an organic acid, the inorganic acid being selected from phosphoric acid, sulfuric acid, sulfamic acid and mixtures thereof, and the organic acid being selected from acetic acid, hydroxyacetic acid, citric acid, tartaric acid, maleic acid, fumaric acid, and mixtures thereof.
11. A composition according to any of claims 1 to 5 wherein the antimicrobial agent is a monocarboxylic acid selected from capric acid, caprylic acid, octanoic acid, decanoic acid, neodecanoic acid, 2,2-dimethyl octanoic acid and mixtures thereof.
12. A composition according to any of claims 1 to 5 wherein the antimicrobial agent is a mixture of mono- and dicarboxylic acids, the monocarboxylic acid being present in a ratio relative to the dicarboxylic acid of between 1:1 to 1:20.
13. A composition according to any of claims 1 to 12 wherein the solubilizer is octamine N,N-dimethyl-N-oxide or decanamine N,N-dimethyl-N-oxide.
14. A composition according to any of claims 1 to 13 wherein the diluent is an anionic material selected from short-chain alcohols having 1 to 3 carbon atoms, and water.
15. A low-foaming aqueous, antimicrobial use solution characterized in that the composition according to any of claims 1 to 14 is diluted in water to provide:
- between 10 and 500 ppm of the selected antimicrobial agent;
  - between 10 and 500 ppm of the solubilizer; and
  - sufficient of the acid to yield a pH below about 5.0.

#### Patentansprüche

1. Antimikrobielle Zusammensetzung, die ihre antimikrobielle Wirkung bei Verdünnung beibehält, dadurch gekennzeichnet, daß sie umfaßt:
- Ein antimikrobielles Mittel, ausgewählt aus einer Monocarbonsäure, einer Dicarbonsäure und ihren Mischungen, wobei die Monocarbonsäure die folgende allgemeine Formel aufweist:



worin  $R'''$  ein geradkettiger oder verzweigt-kettiger, gesättigter oder ungesättigter Alkylrest mit zwischen 6 und 12 Kohlenstoffatomen bedeutet, die Dicarbonsäure die folgende allgemeine Formel aufweist:



- worin R ein gesättigter oder ungesättigter Kohlenwasserstoffrest mit 2 Kohlenstoffatomen ist; R' ein substituierter oder unsubstituierter n-Alkyl- oder n-Alkenylrest ist, wobei jeder n-Alkyl- oder n-Alkenylrest 6 bis 12 Kohlenstoffatome aufweist oder R' Diisobutenyl oder Methylheptenyl ist und R'' eine funktionelle Gruppe ist, ausgewählt aus Wasserstoff und Hydroxy;
- einen Lösungsvermittler, ausgewählt aus einem Alkyl-N,N-dimethylaminoxid-Lösungsvermittler-Kupplungsmittel mit zwischen 8 und 10 Kohlenstoffatomen in seinem Alkylanteil;
  - ein anionisches Verdünnungsmittel und

(d) eine Säure, die in der Lage ist, einen Lösungs-pH von weniger als oder gleich 5,0 bei Verdünnung der Zusammensetzung auf eine gebrauchsfertige Lösung zu ergeben.

2. Zusammensetzung nach Anspruch 1, die folgendes umfaßt:

- (a) 0,25 bis 25,0 Gew.-% des antimikrobiellen Mittels;
- (b) 0,25 bis 40 Gew.-% des Lösungsvermittlers;
- (c) 10,0 bis 95,5 Gew.-% des anionischen Verdünnungsmittels und
- (d) 4,0 bis 50,0 Gew.-% der Säure;

die Prozentzahlen sind auf das Gesamtgewicht der Zusammensetzung bezogen.

3. Zusammensetzung nach Anspruch 1 oder 2, worin je R' ein linearer Kohlenwasserstoff ist.

4. Zusammensetzung nach einem der Ansprüche 1 bis 3, worin je R' zwischen 8 und 10 Kohlenstoffatomen aufweist.

5. Zusammensetzung nach Anspruch 1, worin je R' ein substituierter Rest ist, wobei der Substituent ausgewählt wird aus Thiolgruppen, Methanthiolgruppen, Amingruppen, Methoxygruppen, Arylgruppen und ihren Mischungen.

6. Zusammensetzung nach einem der Ansprüche 1 bis 5, worin die Dicarbonsäure ausgewählt wird aus n-Octylsuccinsäure, n-Octenylsuccinsäure, n-Nonylsuccinsäure, n-Nonenylsuccinsäure, n-Decylsuccinsäure, n-Decenylsuccinsäure, n-Hexylsuccinsäure, n-Hexenylsuccinsäure und ihren Mischungen.

7. Zusammensetzung nach einem der Ansprüche 1 bis 5, worin daß antimikrobielle Mittel ausgewählt wird aus Succinsäure, Maleinsäure und Fumarsäure und ihren Mischungen.

8. Zusammensetzung nach einem der Ansprüche 1 bis 7, worin die Säure eine schwache organische Säure ist, ausgewählt aus Essigsäure, Hydroxyessigsäure, Zitronensäure, Weinsäure, Maleinsäure, Fumarsäure und ihren Mischungen.

9. Zusammensetzung nach einem der Ansprüche 1 bis 7, worin die Säure eine anorganische Säure ist, ausgewählt aus Phosphorsäure, Schwefelsäure, Sulfaminsäure und ihren Mischungen.

10. Zusammensetzung nach einem der Ansprüche 1 bis 7, worin die Säure eine Mischung aus einer anorganischen Säure und einer organischen Säure ist, wobei die anorganische Säure ausgewählt wird aus Phosphorsäure, Schwefelsäure, Sulfaminsäure und ihren Mischungen, und die organische Säure ausgewählt wird aus Essigsäure, Hydroxyessigsäure, Zitronensäure, Weinsäure, Maleinsäure, Fumarsäure, und ihren Mischungen.

11. Zusammensetzung nach einem der Ansprüche 1 bis 5, worin das antimikrobielle Mittel eine Monocarbonsäure ist, ausgewählt aus Caprinsäure, Caprylsäure, Octansäure, Decansäure, Neodecansäure, 2,2-Dimethyloctansäure und ihren Mischungen.

12. Zusammensetzung nach einem der Ansprüche 1 bis 5, worin das antimikrobielle Mittel eine Mischung ist aus Mono- und Dicarbonsäuren, wobei die Monocarbonsäure in einem Verhältnis bezüglich der Dicarbonsäure von zwischen 1:1 bis 1:20 vorliegt.

13. Zusammensetzung nach einem der Ansprüche 1 bis 12, worin der Lösungsvermittler Octamin-N,N-dimethyl-N-oxid oder Decanamin-N,N-dimethyl-N-oxid ist.

14. Zusammensetzung nach einem der Ansprüche 1 bis 13, worin das Verdünnungsmittel ein anionisches Material, ausgewählt aus kurzkettigen Alkoholen mit 1 bis 3 Kohlenstoffatomen, und Wasser ist.

15. Gering schäumende wäßrige antimikrobielle Gebrauchslösung, dadurch gekennzeichnet,

daß die Zusammensetzung gemäß einem der Ansprüche 1 bis 14 in Wasser verdünnt wird, um bereitzustellen:

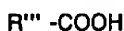
- (a) Zwischen 10 und 500 ppm des ausgewählten antimikrobiellen Mittels;

- (b) zwischen 10 und 500 ppm des Lösungsvermittlers und  
 (c) eine ausreichende Menge der Säure, um einen pH von unter etwa 5,0 zu erzielen.

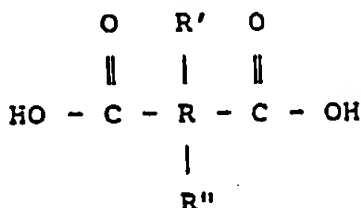
# Revendications

1. Composition antimicrobienne conservant son action antimicrobienne après dilution, caractérisée par le fait qu'elle comporte:

(a) un agent antimicrobien choisi parmi un acide monocarboxylique, un acide dicarboxylique et leurs mélanges, l'acide monocarboxylique ayant la formule générale:



où  $R'''$  est un radical alkyle à chaîne droite ou ramifiée, saturé ou insaturé, contenant entre 6 et 12 atomes de carbone, l'acide dicarboxylique ayant la formule générale :



où R est un radical hydrocarboné, saturé ou insaturé, contenant 2 atomes de carbone;  $R'$  est un radical n-alkyle ou n-alkényle, substitué ou non, chaque radical n-alkyle ou n-alkényle contenant 6 à 12 atomes de carbone, ou bien  $R'$  est le radical diisobutényle ou méthylheptényle; et  $R''$  est un groupe fonctionnel choisi parmi l'hydrogène et le groupe hydroxyle;

(b) un agent solubilisant choisi parmi un agent de couplage solubilisant du type oxyde de N,N-diméthylamine alkylée contenant entre 8 et 10 atomes de carbone dans la partie alkyl ;

(c) un diluant anionique, et

(d) un acide capable de donner un pH de solution inférieur ou égal à 5,0 après dilution de la composition pour donner une solution prête à l'emploi.

2. Composition selon la revendication 1, comportant:

(a) de 0,25 à 25,0 pour-cent, en poids de l'agent antimicrobien;

(b) de 0,25 à 40 pour-cent, en poids, de l'agent solubilisant;

(c) de 10,0 à 95,5 pour-cent, en poids, du diluant anionique; et

(d) de 4,0 à 50,0 pour-cent, en poids, de l'acide; les pourcentages étant basés sur le poids total de la composition.

3. Composition selon la revendication 1 ou la revendication 2, dans laquelle chaque  $R'$  est un hydrocarbure linéaire.

4. Composition selon l'une quelconque des revendications 1 à 3 dans laquelle chaque  $R'$  contient entre 8 et 10 atomes de carbone.

5. Composition selon la revendication 1 dans laquelle chaque  $R'$  est un radical substitué, le substituant étant choisi parmi les groupes thiol, les groupes méthane thiol, les groupes amine, les groupes méthoxy, les groupes aryle et leurs mélanges.

6. Composition selon l'une quelconque des revendications 1 à 5, dans laquelle l'acide dicarboxylique est choisi parmi l'acide n-octylsuccinique, l'acide n-octénylsuccinique, l'acide n-nonylsuccinique, l'acide n-nonénylsuccinique, l'acide n-décylsuccinique, l'acide n-décénylsuccinique, l'acide n-héxylsuccinique, l'acide n-héxénylsuccinique, et leurs mélanges.

7. Composition selon l'une quelconque des revendications 1 à 5, dans laquelle l'agent microbien est choisi parmi l'acide succinique, l'acide maléique, l'acide fumarique et leurs mélanges.

8. Composition selon l'une quelconque des revendications 1 à 7, dans laquelle l'acide est un acide organique faible choisi parmi l'acide acétique, l'acide hydroxyacétique, l'acide citrique, l'acide tartrique, l'acide maléique, l'acide fumarique et leurs mélanges.
- 5 9. Composition selon l'une quelconque des revendications 1 à 7, dans laquelle l'acide est un acide inorganique choisi parmi l'acide phosphorique, l'acide sulfurique, l'acide sulfamique et leurs mélanges.
- 10 10. Composition selon l'une quelconque des revendications 1 à 7 dans laquelle l'acide est un mélange d'un acide inorganique et d'un acide organique, l'acide inorganique étant choisi parmi l'acide phosphorique, l'acide sulfurique, l'acide sulfamique et leurs mélanges et l'acide organique étant choisi parmi l'acide acétique, l'acide hydroxyacétique, l'acide citrique, l'acide tartrique, l'acide maléique, l'acide fumarique et leurs mélanges.
- 15 11. Composition selon l'une quelconque des revendications 1 à 5 dans laquelle l'agent anti-microbien est un acide monocarboxylique choisi parmi l'acide caprique, l'acide caprylique, l'acide octanoïque, l'acide décanoïque, l'acide néodécanoïque, l'acide 2,2-diméthyl-octanoïque et leurs mélanges.
- 20 12. Composition selon l'une quelconque des revendications 1 à 5, dans laquelle l'agent anti-microbien est un mélange d'acides monocarboxylique et d'acide dicarboxylique, l'acide monocarboxylique étant présent dans une proportion par rapport à l'acide dicarboxylique comprise entre 1:1 et 1:20.
13. Composition selon l'une quelconque des revendications 1 à 12 dans laquelle l'agent solubilisant est la N,N-diméthyl-N-oxyde octamine ou la N,N-diméthyl-N-oxyde décanamine.
- 25 14. Composition selon l'une quelconque des revendications 1 à 13 dans laquelle le diluant est un produit anionique choisi parmi les alcools à courte chaîne contenant de 1 à 3 atomes de carbone et l'eau.
- 30 15. Solution antimicrobienne, aqueuse, faiblement moussante, prête à l'emploi, caractérisée par le fait que la composition selon l'une quelconque des revendications 1 à 14 est diluée dans l'eau pour contenir:
  - (a) entre 10 et 500 ppm de l'agent antimicrobien choisi;
  - (b) entre 10 et 500 ppm de l'agent solubilisant; et
  - (c) suffisamment d'acide pour donner un pH inférieur à environ 5,0.